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Triplet and higher correlations of liquid rubidium and mercury in the long wavelength limit

R. V. Gopala Rao and D. Sen

Department of Chemistry, Jadavpur University, Calcutta-700032

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The nth order structures of a liquid, defined as the ensemble average of a product of n Fourier components of the atomic density, is studied in the limit of long wavelength for one or more Fourier components. Ballentine & Lakshmi (1975), using the theory of fluctuations have shown that these limits are simply related to lower order structure functions and their derivatives with respect to pressure. Values of these quantities calculated on the basis of perturbation treatment of Percus-Yevick equation are in good agreement with experiment.

1. Theory

Ballentine & Lakshmi (1975) have shown that the n-th order structure functions is related to the $(n-1)$ th order structure function in the limit $K_n \to 0$ as follows

$$S_n(K_1, K_2, \ldots, K_{n-1}, 0)$$

$$= \rho k_B T \left[\frac{\partial S_{n-1}(K_1, K_2, \ldots, K_{n-1})}{\partial \rho^{n-1}} \right]_T + S_2(0).S_{n-1}(K_1, K_2, \ldots, K_{n-1}) \quad \ldots \quad (1)$$

where ρ is the no. density $(= N/V)$.

At present we have sufficient information to calculate $S_n(K_1, K_2, \ldots, K_{n-1}, 0)$ for $n = 3$,

$$S_3(K, -K, 0) = \rho k_B T \left[\frac{\partial S_2(K)}{\partial \rho} \right]_T + S_2(0).S_2(K) \quad (2)$$

and for $n = 4$ in a limiting case,

$$S_4(K, -K, 0, 0) = (\rho k_B T)^2 \left[\frac{\partial^2 S_2(K)}{\partial \rho^2} \right]_T + \rho k_B T$$

$$\times \left\{ S_2(K). \left[\frac{\partial S_2(0)}{\partial \rho^2} \right]_T + 3S_2(0). \left[\frac{\partial S_2(K)}{\partial \rho} \right]_T \right\} + [S_2(0)]^2. S_2(K). \quad \ldots \quad (3)$$

Taking square well potential as perturbation over hard sphere potential solution of Percus-Yevick equation, Rao & Sen (1976) have deduced an expression for the

Fourier transform of the total correlation function, $C(r)$. using that expression, we can show that

$$S_2(0) = [\alpha - 8\eta\epsilon(\lambda^3-1)/(k_BT)]^{-1} \quad \ldots (4)$$

where $\eta = \pi\rho\sigma^3/6$, σ being the so called hard sphere diameter, $\alpha = (1+2\eta)^2/(1-\eta)^4$, λ and ϵ are square well parameters.

Using the so-called $\rho^{-1/3}$ model of Egelstaff *et al* (1971), Rao & Murthy (1975, 1976) have deduced expressions for

$$\rho k_BT \left[\frac{\partial S_2(K)}{\partial P}\right]_T \text{ and } (\rho k_BT)^2 \left[\frac{\partial^2 S_2(K)}{\partial P^2}\right]_T$$

using these expressions along with eqs. (1)–(4) and the expressions deduced by Rao & Sen (1976), we can calculate $S_3(K, -K, 0)$ and $S_4(K, -K, 0, 0)$ as functions of K. Ballentine & Lakshmi (1975) have also shown that

$$S_3(0, 0, 0) = [S_2(0)]^2 \times \left\{2+\beta_T{}^{-2}\left[\frac{\partial\beta_T}{\partial\rho}\right]_T\right\} \quad \ldots (5)$$

and

$$S_4(0, 0, 0, 0) = [S_2(0)]^3 \times \left\{6+7\beta_T{}^{-2}\left[\frac{\partial\beta_T}{\partial P}\right]_T + \beta_T{}^{-3}\left[\frac{\partial^2\beta_T}{\partial P^2}\right]_T\right\} \quad \ldots (6)$$

where β_T is the isothermal compressibility which is related to $S_2(0)$as :

$$S_2(0) = \rho k_BT\beta_T \quad \ldots (7)$$

using eqs. (4)–(7), we can easily show that

$$S_3(0, 0, 0) = [S_2(0)]^2 \times [2 - S_2(0) \times \times \{(1+2\eta)(1+9\eta+2\eta^2)/(1-\eta)^5 - 16\}\epsilon/(k_BT)\{\eta(\lambda^3-1)\}] \quad \ldots (8)$$

and

$$S_4(0, 0, 0, 0) = [S_2(0)]^3 \times [6 - 8S_2(0) \times \times \{(1+2\eta)(1+9\eta+2\eta^2)/(1-\eta)^5 - 16\{\epsilon/(k_BT)\}\eta(\lambda^3-1)\} + 3[S_2(0)]^2 \times \{(1+2\eta)(1+9\eta+2\eta^2)/(1-\eta)^5 - 16\}\epsilon/(k_BT)\{\eta(\lambda^3-1)\}^2 - \eta S_2(0)\{(16+84\eta+72\eta^2+8\eta^3)/(1-\eta)^6 - 16\{\epsilon/(k_BT)\} \times (\lambda^3-1)\}] \quad \ldots (9)$$

thus we can calculate $S_3(0, 0, 0)$ and $S_4(0, 0, 0, 0)$ by knowing the parameters σ, λ and ϵ/k_B.

2. Results and Discussions

$S_3(K, -K, 0)$ and $S_4(K, -K, 0, 0)$ are calculated using eqs. (2) and (3). The potential parameters used are those determined by Rao & Murthy (1974,

1975) by fitting experimental $S_2(K)$ data at first peak position and are shown in table 1. $S_3(K, -K, 0)$ and $S_4(K, -K, 0, 0)$ are shown in figures 1 and 2. Results on Rb are in good agreement with experimental values of Ballentine & Lakshmi (1975). Unfortunately there are no experimenoal data in the case of mercury to compare with the calculated values. $S_3(0, 0, 0)$ and $S_4(0, 0, 0, 0)$ calculated by using eqs. (8) and (9) are shown in table 2 with experimental values of Bridgeman (1911) and Davis & Gordon (1967) and hard sphere calculations of Ballentine & Lakshmi. (1975).

Table 1. Potential parameters used for liquid mercury and rubidium.

Liquid metal	Temp. (°K)	σ (Å)	ϵ/K_B (°K)	λ	ρ atom Å^{-3}
Mercury	295	2·8	100	1·73	0·04097
Rubidium	333	4·306	96·14	1·65	0·010716

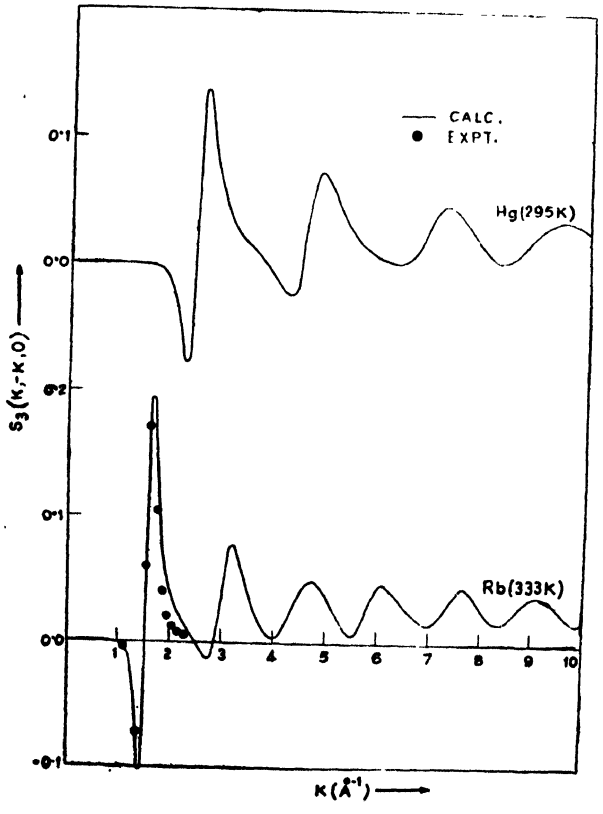

Fig. 1. $S_3(K, -K, 0)$ vs. K curve for Rb and Hg along with experimental values.

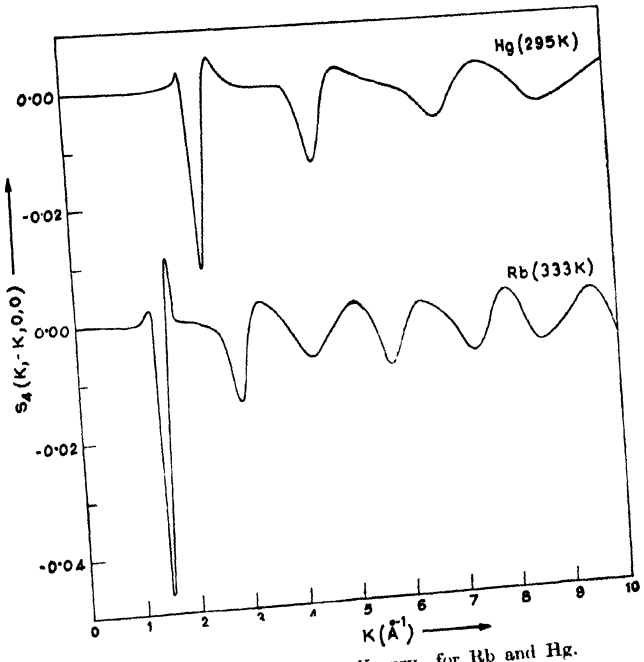

Fig. 2. $S_4(K, -K, 0)$ vs. K curve for Rb and Hg.

Table 2. Calculated and experimental values of 2nd, 3rd and 4th order structure functions of liquid mercury and rubidium in the long wavelength limit.

	Rubidium		Mercury		
	Present work	Present work	Hard sphere	Bridgeman	Gordon & Davis
$S_2(0)$	0·028493	0·023374	0·025348	0·0067	0·00666
$S_3(0, 0, 0)$	−0·002857	−0·002169	−0·002069	-2×10^{-4}	$-3{\cdot}2\times10^{-4}$
$S_4(0, 0, 0, 0)$	0·000518	0·000371	0·000285	-3×10^{-5}	$5{\cdot}1\times10^{-5}$

References

Ballentine L. E. & Lakshmi A. 1975 *Can. J. Phys.* **53**, 372.

Bridgeman P. W. 1911 *Proc. Am. Acad. Arts. Sci.* **47**, 345.

Davis L. A. & Gordon R. B. 1967 *J. Chem. Phys.* **46**, 2650.

Egelstaff P. A., Page D. I. & Heard C. R. T. 1971 *J. Phys. C : Solid State Phys.* **4**, 1453.

Rao R. V. G. & Sen D. 1976 *Ind. J. P. Appl. Phys.* **14**, 853.

Rao R. V. G. & Murthy A. K. 1974 *Phys. Stat. Sol.* (*b*) **66**, 703.

Rao R. V. G. & Murthy A. K. 1975 *Chem. Phys. Letts.* **31**, 605.

Rao R. V. G. & Murthy A. K. 1976 *Ind. J. Phys.* **50**, 000.

Rao R. V. G. & Murthy A. K. 1975 *Z. Naturforsch.* **30a**, 619.